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13. ABSTRACT (Maximum 200 Words) Photoassisted poling of azobenzene containing polymer films at room temperature using polarized Ar ⁺ laser beam as pump light was studied. Irradiating the films with <i>p</i> -polarized pump light at an incident angle to the normal during the poling process, second harmonic generation with in-plane anisotropy could be induced. Second order nonlinear optical coefficient, <i>d</i> ₃₃ , of the poled sample was measured to be 20 pm/V. The second harmonic generation properties induced by photoassisted poling and thermal assisted poling were compared.				
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Photoassisted poling induced second harmonic generation with in-plane anisotropy in azobenzene containing polymer films

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Photoassisted poling of azobenzene containing polymer films at room temperature using polarized Ar^+ laser beam as pump light was studied. Irradiating the films with *p*-polarized pump light at an incident angle to the normal during the poling process, second harmonic generation with in-plane anisotropy could be induced. Second order nonlinear optical coefficient, d_{33} , of the poled sample was measured to be 20 pm/V. The second harmonic generation properties induced by photoassisted poling and thermal assisted poling were compared.

During the past decade second-order nonlinear optical (NLO) polymeric materials have attracted a lot of attention due to their potential application in electro-optic modulation and frequency doubling devices.^{1, 2} To achieve the second-order NLO properties in the polymer films, poling techniques have to be used to induce the required noncentrosymmetry. A poling technique, commonly referred to as thermally assisted poling (TAP), involves heating a sample to an elevated temperature (close to the glass transition temperature (T_g) of the polymer), applying a high electric field for a period of time and subsequently cooling the sample back to room temperature and removing the field.³⁻⁵

Recent studies have demonstrated that photoassisted poling (PAP) of azobenzene containing polymer films at room temperature is possible.⁶⁻¹⁰ The trans-cis-trans photoisomerization of azobenzene groups is considered to be the mechanism for PAP technique. On exposure to light within the absorption band of the trans-isomer, azobenzene groups could transform from the trans-isomer to the cis-isomer, which is more compact and can tumble more easily than the trans-isomer, and the cis-isomer would relax back to the trans-isomer. Due to the trans-cis-trans cycling, the azobenzene groups are preferentially aligned. By applying a small dc electric field during the photoisomerization process, the centrosymmetry in the films can be broken at room temperature and second-order NLO susceptibility is induced. It is known that during the trans-cis-trans photoisomerization process, the polarization of light strongly influences the orientation of azobenzene groups.^{11,12} It is expected that the orientation of net dipole moment obtained in the PAP should be affected by the polarization of pump light as well. Our studies using the PAP technique on an azobenzene containing polymer indicate that large second harmonic generation (SHG) with in-plane anisotropy can be produced by irradiating the sample with *p*-polarized laser beam at an incident angle. To the best of our knowledge, it is the first time

this behavior has been reported.

An epoxy-based polymer from diglycidyl ether of bisphenol A and 4-(4'-nitrophenylazo) phenyl amine and functionalized with UV photocrosslinkable methacryloyl groups was used in this study. The polymer was synthesized according to ref. 13. The chemical structure, characterization and novel optical processing properties of this polymer are described elsewhere.¹³⁻¹⁶ The T_g of the polymer is 115°C. The polymer was dissolved in propylene glycol methyl ether acetate and 1,4-dioxane (volume ratio 3:1) with a weight ratio of 1:10. The solution was spin-coated on glass slides and then baked at 70°C under vacuum for 12 hours. The typical thickness of the film is 0.4 μm .

A corona poling apparatus with needle-to-plane arrangement^{3, 4} was used for the PAP study. The voltage between a thin tungsten wire (3 mm above the sample) and the grounded sample was adjusted within 2-4 kV. The experimental setup for the PAP study is shown in Fig. 1. The polymer films were irradiated by a *p*-polarized pump beam at 488 nm from an Ar⁺ laser at an incident angle of θ . The values for θ were chosen to be 0°, 35°, and 65°. The SHG technique was used as an *in-situ* probe for the PAP process with a *p*-polarized fundamental beam at 1.064 μm from a Q-switched Nd:YAG laser. For SHG measurement, only *p*-polarized second harmonic (SH) intensity was recorded. In order to compare the PAP and TAP, a sample was poled following the steps and conditions of TAP described in ref. 14.

A typical PAP sequence is shown in Fig. 2. Application of the dc electric field gave rise to a small SH intensity, which is mainly due to electric field induced second harmonic generation (EFISH). During the PAP process (solid curve), the small decrease during the first stage could be attributed to the decay of the electrostatic charges on the polymer film. When the pump beam was switched on, an initial drop in SH intensity was observed. This is expected, since

the photoinduced isomerization process would initially partially randomize the dc field aligned azobenzene groups.¹⁰ Continuous cycling of the dipoles through the trans-cis-trans photoisomerization under the dc field eventually lead to their alignment even at room temperature. This increase in alignment gave rise to a large increase in SH intensity in the following 2 minutes. In the third stage, the pump beam was switched off, the photoisomerization stopped and the azobenzene groups in the cis-isomer thermally relaxed to the trans-isomer while oriented by the dc field. Upon removal of the dc field, rapid drop in SH intensity resulted from the disappearances of EFISH and possibly some trapped charges. The dotted line in Fig. 2 shows how SH intensity developed without pump irradiation.

The SHG behavior of the samples poled by PAP technique with pump beam at different incident angle θ were studied after the dc field was removed. Fig. 3 displays the SH intensity as a function of the incident angle (ϕ) of the fundamental beam for the samples poled with the pump beam at 0° , 35° and 65° . The sample poled at $\theta=0^\circ$ shows SHG behavior similar to the sample poled by the TAP technique. Its SH intensity is symmetric with respect to ϕ and vanishes at normal incidence. However, the samples poled at $\theta=35^\circ$ and $\theta=65^\circ$ exhibit non zero SHG at normal incident angle. The SH intensity with respect to ϕ is asymmetric with minimum SH intensity occurring at $\phi=6^\circ$ for the sample poled at $\theta=35^\circ$ and $\phi=10^\circ$ for the sample poled at $\theta=65^\circ$.

The dependence of SH intensity for the sample poled at $\theta=65^\circ$ on the polarization of the fundamental beam with normal incidence is shown in Fig. 4. The maximum or minimum SH intensity is obtained when the polarization of fundamental and SH beams are parallel or perpendicular to each other. The effective d value correspondent to the maximum SH intensity in Fig. 4 is about 1.9 pm/V. A very good fit for a function of $(A+B\cos(2\phi))^2$, with non zero A, B, clearly indicates that there is an in-plane anisotropy or in-plane component of

the net induced polarization at double frequency.

This interesting result can be explained in terms of the trans-cis-trans isomerization of azobenzene groups. Fig. 5 illustrates the directions of the dc electric field, the polarization of the pump light and the net dipole moment. It is known that an azobenzene group would undergo repeated trans-cis-trans cycling until its orientation is perpendicular to the polarization of pump beam.^{11, 12} In the case of $\theta=0^\circ$, the pump beam polarization is perpendicular to the dc field and azobenzene groups aligned in the direction of the dc field are inert to the photoisomerization process, thus the net dipole moment obtained in the film would be in the same direction as the dc field. However, in the cases of $\theta \neq 0^\circ$, the dc field is not perpendicular to the polarization of pump beam. The dipole orientations preferred by photoisomerization and the interaction of the dc field with the dipoles are no longer coincident. The final steady-state distribution of the dipoles, which is determined by the two competitive processes, has a net dipole moment oriented in the direction between the dc field and the propagation direction of the pump beam.

Usually, the second order nonlinear polarization and net dipole moment of the polymer film poled by TAP are in the same direction as the poling field and no SHG could be observed as the fundamental beam propagates along this direction. As discussed earlier, for PAP with the pump beam at $\theta \neq 0^\circ$, the net dipole moment of the poled polymer film is not in the same direction as the poling field. Assuming in these samples the SH intensity reaches the minimum as the fundamental beam propagates along the direction of the net dipole moment, from the result in Fig. 3, we evaluated the azimuth angle of the net dipole moment or second order polarization to be about 3.5° in samples poled at $\theta=35^\circ$ and 6.0° in sample poled at $\theta=65^\circ$ respectively.

In addition to the *p*-polarized pump light, the polymer films were also

irradiated with *s*-polarized and circularly polarized pump light at $\theta=0^\circ$. These samples exhibited the same SHG properties as the sample irradiated with *p*-polarized pump light at $\theta=0^\circ$. The d_{33} value of the sample poled by PAP at $\theta=0^\circ$ is about 20 pm/V. This value is approximate half of the d_{33} value (=47 pm/V) of the TAP poled sample.¹⁴ The temporal behavior of SHG from the sample poled by PAP was also studied. The SH intensity of the sample is relaxed to 65% of the original value within 150 hours after poling. This stability is comparable to that obtained from TAP.¹⁴

The decay of SHG from the samples poled by TAP and PAP on exposure to the Ar⁺ laser beam was monitored. SHG from the samples poled by TAP and PAP were observed to decrease as shown in Fig 6. The fast decay of SH intensity is certainly attributed to the photoisomerization, which would cause the reorientation of azobenzene groups and the randomization of dipoles alignment in the film. It is interesting to note that after irradiating the samples, SHG from the photoassisted poled sample totally vanished but ~25% SH intensity was measured for the thermally assisted poled sample. The results suggests that in PAP process, primarily azobenzene groups are reoriented and this change is completely reversible by light. However, during the TAP process, not only are azobenzene group oriented, but realignment and densification of main chains also occurs.^{3, 4, 7} The densification of the polymer results in reduced free volume and thus the orientation of azobenzene groups is locked in place unless the polymer is reheated to its T_g.

In conclusion, we demonstrated that large and relatively stable second order NLO properties can be induced in a azobenzene containing polymer by PAP. Due to the photoinduced orientation of azobenzene groups during the PAP process, a net in-plane component of second order polarization could be obtained by using a *p*-polarized pump light at an incident angle. It was found that the

alignment of the net dipole moment produced by PAP can be totally randomized by irradiating the poled sample with the same laser beam.

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Figure Caption

Fig. 1 Experimental setup for the PAP study.

Fig. 2 SH intensity as a function of time during PAP (solid line) with the pump beam at $\theta=0^\circ$ and the poling process without pump beam (dotted line) at room temperature.

Fig. 3 SH intensity as a function of incident angle of the fundamental beam for the samples poled at various angles. The inset shows the detail at small incident angle.

Fig. 4 Dependence of SH intensity on the polarization of fundamental beam at normal incidence angle for the sample poled at $\theta=65^\circ$.

Fig. 5 Relations among the directions of light polarization, dc electric field and the net dipole moment during the PAP process.

Fig. 6 Fast decay of SH intensity upon irradiation of the samples poled by PAP (solid line) and TAP (dotted line) with 488 nm laser light.

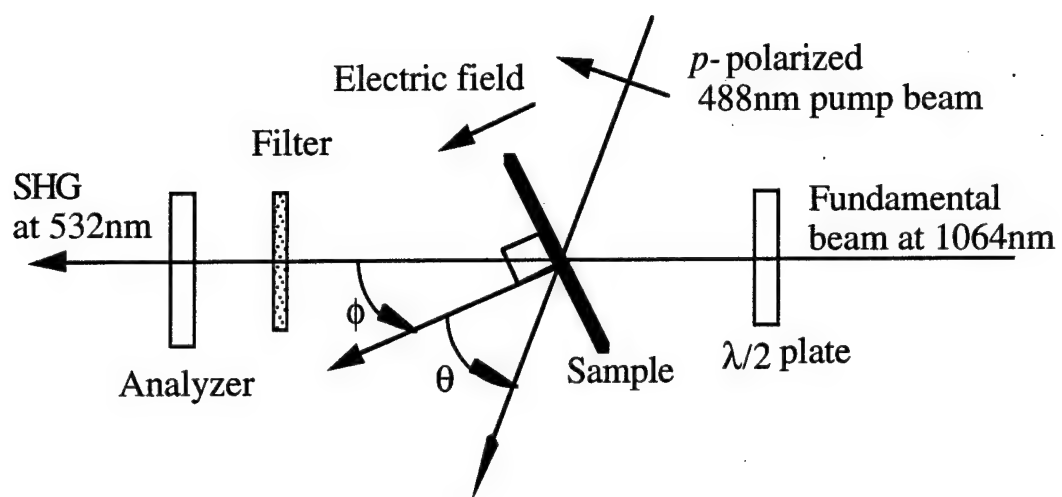


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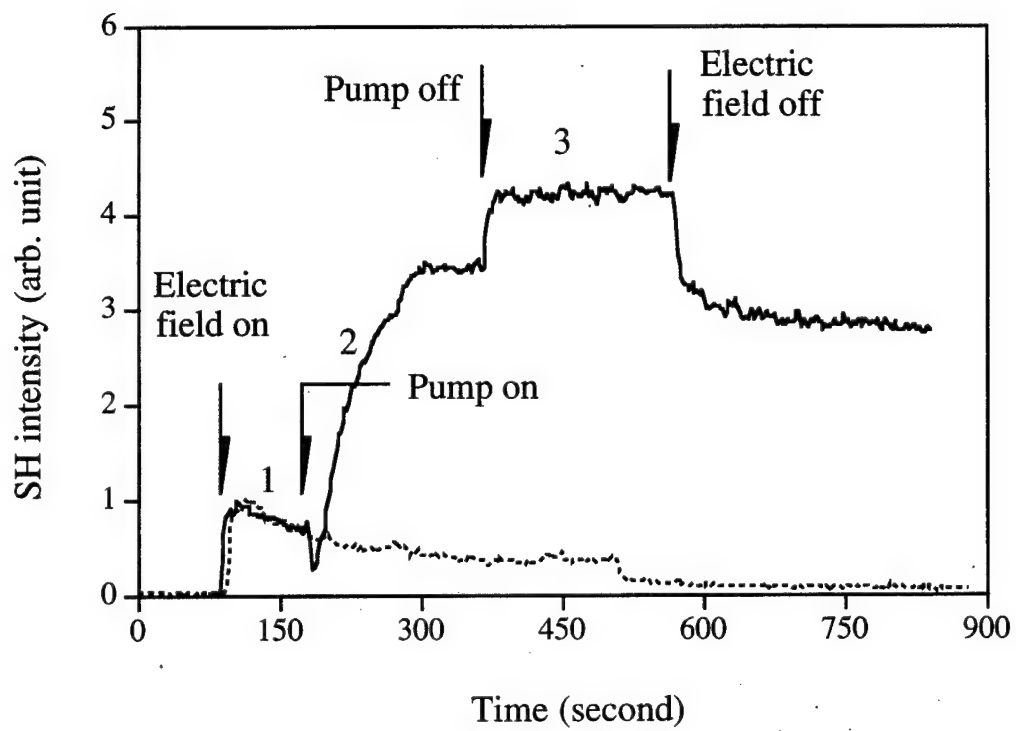


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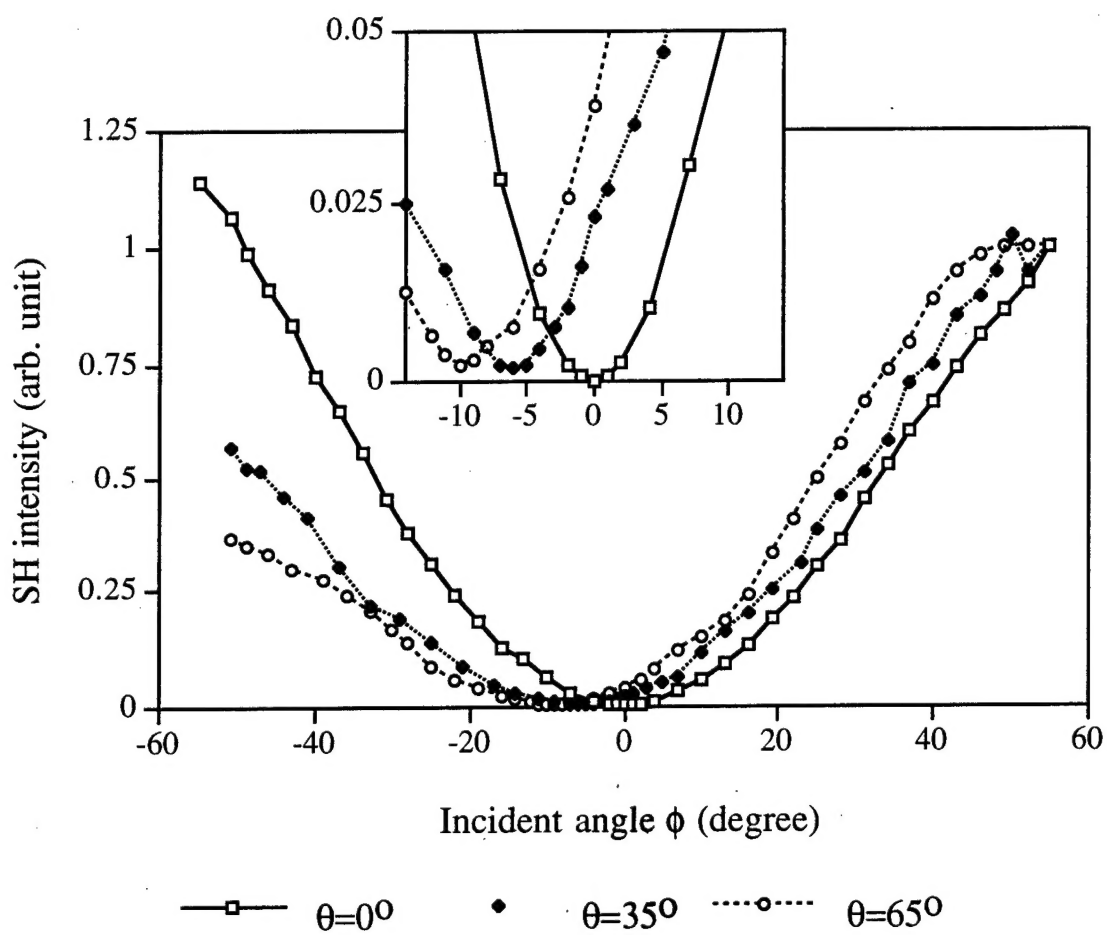


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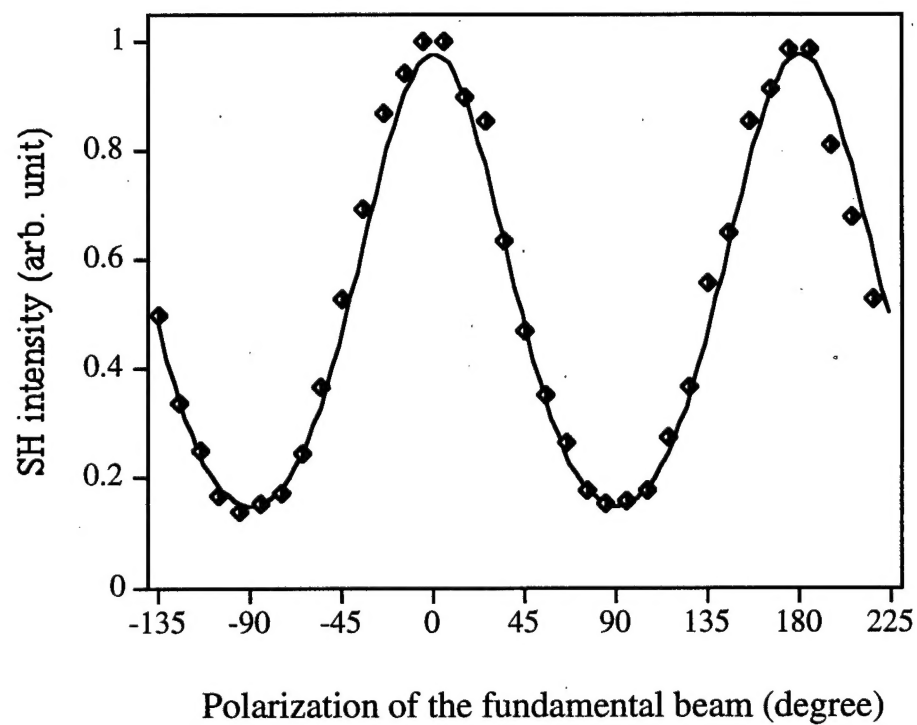


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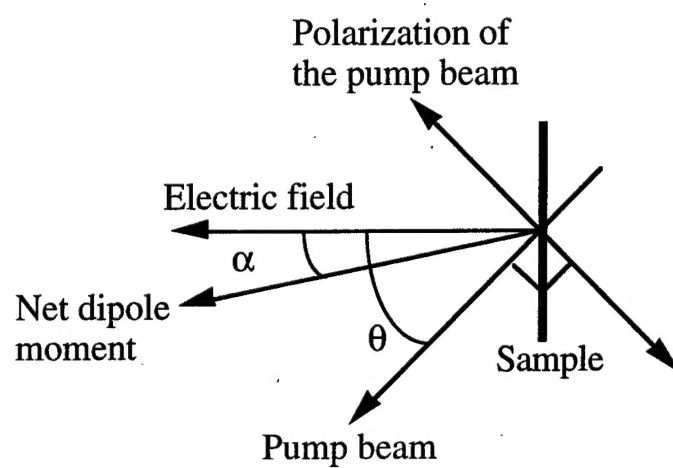


Fig. 5, X. L. Jiang, Appl. Phys. Lett.

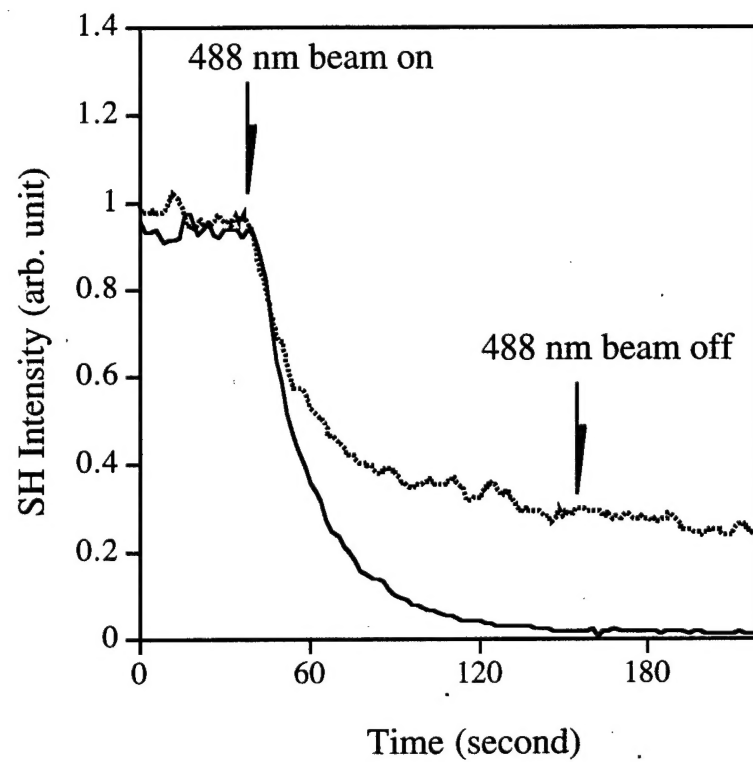


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